Carpathian Journal of Earth and Environmental Sciences, February 2015, Vol. 10, No. 1, p. 147 - 160

TRACE ELEMENTS CONTENTS AND ACCUMULATION IN SOILS AND PLANT SPECIES *GONIOLIMON TATARICUM* (L.) BOISS. (PLUMBAGINACEAE) FROM THE ULTRAMAFIC AND DOLOMITIC SUBSTRATES OF THE CENTRAL BALKANS

Ksenija JAKOVLJEVIĆ[1*], Uroš BUZUROVIĆ[1], Gordana ANDREJIĆ[1], Sanja ĐUROVIĆ[1], Marjan NIKETIĆ[2], Nevena MIHAILOVIĆ[3] & Gordana TOMOVIĆ[1]

[1]*Institute of Botany and Botanical Garden, Faculty of Biology, University of Belgrade, Takovska 43, 11000 Belgrade, Serbia*
[2]*Natural History Museum, Njegoševa 51, 11000 Belgrade, Serbia*
[3]*Institute for the Application of Nuclear Energy – INEP, University of Belgrade, Banatska 31b, 11080 Belgrade, Serbia*
e-mail: kjakovljevic@bio.bg.ac.rs, uros_buzurovic@yahoo.com, 1988xg@gmail.com, sdjurovic@bio.bg.ac.rs, mniketic@nhmbeo.rs, nmihailovic@inep.co.rs, gtomovic@bio.bg.ac.rs
**corresponding author: kjakovljevic@bio.bg.ac.rs*

Abstract. Potential for trace elements accumulation of the species *Goniolimon tataricum* (L.) Boiss.was estimated. Plant tissues of *Goniolimon tataricum* and associated soils were sampled from four sites in Serbia and Republic of Macedonia located on two different geological substrates (ultramafics and dolomites). The aims of the present study were to investigate the levels of P_2O_5, K_2O, Ca, Mg, Fe, Mn, Ni, Zn, Co, Cr, Cu, Cd and Pb in the soils and plant tissues of *G. tataricum* from these four localities. Soil samples collected from ultramafics contained elevated levels of almost all analysed trace elements and Ca/Mg quotients for the available fraction are close to 1. As for the dolomitic samples, they were characterized by elevated levels of Cd, Mn, Pb, Zn, Ca, and remarkably high Ca/Mg ratio. In plant tissues of *G. tataricum* remarkably high concentrations of Mg, Cu and Cr were measured (up to 16584, 321 and 71.4 mg/kg, respectively). This survey suggests that some *G. tataricum* populations from the ultramafic and dolomite soils of Serbia and the Republic of Macedonia emerge as Cu and Cr accumulators and could be used for phytoextraction purposes.

Key words: *Goniolimon tataricum*, ultramafics, dolomites, trace elements, accumulation, Central Balkans

1. INTRODUCTION

Ultramafic rocks (serpentinite, peridotite, dunite) are known for a long time as a strongly hostile environment (Brooks, 1987; Baker et al., 1992; Roberts & Proctor, 1992). These ecosystems fascinated many botanists because of the unique flora they support, which due to some adaptive structures and functions managed to thrive on this demanding substrate. Although patchily distributed all over the world, they cover only 1% of the world's surface (Sequeira & Pinto da Silva, 1992). Some of the ultramafic areas can be found in the United States, Canada, Brazil, Cuba, SE Asia, S Africa, and Europe. In Europe, in addition to relatively small areas located in the Sweden, Norway, Czech, Switzerland, Great Britain, Portugal, and Italy, the largest ultramafic zones are in the Balkan Peninsula. According to Stevanović et al., (2003), in the Balkans ultramafics (serpentinite) exists in large blocks or as small outcrops in C Bosnia, W&C Serbia, and C&SE Albania, ending at the ultramafic formations of Epirus, Thessaly and island Euboea in Greece. Small surfaces also occur in SW&C Bulgaria, mainly in E&C Rhodope (Pavlova et al., 1998; Pavlova, 2001).

Increased interest in edaphic flora, started with ultramafic explorations and led to intensive studies of other types of substrate. However, little work has been done on dolomites. Dolomite is similar to ultramafics, having a high concentration of magnesium, although it’s origin is related to limestone. While limestone is mainly composed of calcium carbonate, dolomite is usually composed of calcium carbonate and magnesium carbonate, wherein the magnesium can be replaced with iron or, rarely, manganese (Wyckoff & Merwin, 1924). McHale & Winterhalder (1997) assigned the terms ”calcitic limestone” to one kind of rock and ”dolomitic limestone” to the other. Pure dolomite, although very rare, can contain even 45% of $MgCO_3$. Considering the replacement of magnesium with iron in dolomite, Palache et al., (1951) recommended that the name dolomite should refer to the rocks containing more magnesium then iron, oppose to ankerite, containing more iron than magnesium. Metamorphism of carbonate minerals (calcite, dolomite and/or aragonite) results in marble, metamorphic rock that contains more than 50% volume of carbonate minerals. Depending on whether there are more than 95% of carbonate minerals, marbles can be classified as pure or impure (Rosen et al., 2011). In Serbia, the largest dolomite and marble areas can be found in western (Mt Zlatibor, Čačak, etc.), eastern (surroundings of Pirot and Prokuplje) and central parts (Mt Venčac) (Pefrov, 1980; Đorđević et al., 1991). Soils derived from calcareous bedrock (such as dolomite or limestone) are generally fine textured and neutral to slightly alkaline (Donahue et al., 1977) with low concentrations of certain plant nutrients (N, P, K) and high concentrations of $MgCO_3$ (Neely & Barkworth, 1984).

However, in ultramafic soils, this is just a part of the harsh conditions for plant growth. In addition to low concentration of many essential nutrients such as P, K, and Ca, ultramafic soils generally have high contents of heavy metals such as Fe, Ni, Co, Cr (Kruckeberg, 1984; Walker, 2001). They are characterized by low Ca/Mg ratios, generally < 1, with Ca at significantly lower concentrations relative to surrounding areas and toxic concentration of Mg (Bradshaw, 2005; Brady et al., 2005; Skinner, 2005). All this, associated with soil xericity, limits the plant growth (Brooks, 1987; Roberts & Proctor, 1992), resulting in the uniqueness of ultramafic soils and the plant species they support.

Since these soils contain phytotoxic concentrations of several trace elements, many of the well-adapted plants represent hyperaccumulators. According to Baker & Brooks (1989), hyperaccumulators are defined as plants with more than 1000 µg/g dry weight of Ni, Co, Cu, Cr, or Pb, or more than 10,000 µg/g dry weight of Zn or Mn in their tissues. Most of hyperaccumulators belong to the family Brassicaceae. Particularly intensive research was done on the *Alyssum* L. species, especially sect. *Odontarrhena* C. A. Mey., known as a group of plants with the highest number of Ni hyperaccumulators. Previous studies of heavy metal accumulation in the territory of Serbia were also related mainly to the representatives of Brassicaceae, particularly *Thlaspi* L. and *Alyssum* species (Vinterhalter & Vinterhalter, 2005; Vinterhalter et al., 2008; Tumi et al., 2012; Tomović et al., 2013), rarely to the representatives of other families, like Hypericaceae (Obratov-Petković et al., 2008), Lamiaceae, Apiaceae and Cistaceae (Dudić et al., 2007).

Regarding the family Plumbaginaceae, previous research was related only to the genus *Armeria* Willd., especially to *Armeria maritima* (Mill.) Willd., that was recognized many years ago as an indicator of high heavy metal contents in soil. First of all, Henwood (1857) reported that the presence of copper in the Wales was indicated by growth of this species. This was followed by the research of tolerance and accumulation of different trace elements (Zn, Cu, Pb etc.) in metal-tolerant taxa included in the *A. maritima* complex (Ernst, 1974, 1982, 1998; Farago et al., 1980; Neumann et al., 1995). In addition, it was pointed out that ecotype differentiation is induced primarily by chemical conditions of soil (Lefebvre, 1974; Goodwin-Bailey et al., 1992; Kőhl, 1997; Abratowska et al., 2012). In this respect, *Armeria maritima* (Mill.) Willd. ssp. *halleri* (Wallr.) A & D. Löve was described from the different mining region as endemic metallophyte and characteristic species of the calamine flora among other, like *Biscutella laevigata*, *Dianthus carthusianorum*, *Silene vulgaris* (Rostański & Wierzbicka, 2002).

Best to our knowledge, there are no studies concerning trace elements tolerance and accumulation in *Goniolimon* species. Genus *Goniolimon* Boiss. comprises about 20 species distributed from North Africa (Algeria, Tunisia), across Europe and Russia to Mongolia (Linčevski, 1952). The center of diversity lies in the Mediterranean area, Macaronesia and Europe (Greuter et al., 1989). There are no records of *Goniolimon* occurring on ultramafics, except in the Central Balkans, and hence there was no investigation of hyperaccumulation potentials of the species. Previous studies in this region were related primarily to the distribution, and resulted in knowledge that there is only one species on the territory of Serbia - *Goniolimon tataricum* (L.) Boiss. (Buzurović et al., 2013) and two species in the Republic of Macedonia - *Goniolimon tataricum* and *Goniolimon dalmaticum* (C. Presl) Reichenb.fil. (Micevski & Matevski, 1995).

The objectives of this study were: 1) to investigate the level of P_2O_5, K_2O, Ca, Mg, Fe, Mn, Ni, Zn, Cr, Cu, Co, Cd and Pb in the soils from several ultramafic localities and one dolomitic site of *G. tataricum*; 2) to examine the level of accumulation of these elements in plant tissues (roots and shoots) and test the *G.tataricum* capability to hyperaccumulate some of the them; 3) to compare the level of accumulation of these elements in the plant tissues among localities with different geological substrate (ultramafics and dolomitic).

2. MATERIAL AND METHODS

Plant samples of *Goniolimon tataricum* and associated soil were sampled in four sites located on two different geological substrates (ultramafics and dolomitic) for the essential and trace elements analyses.

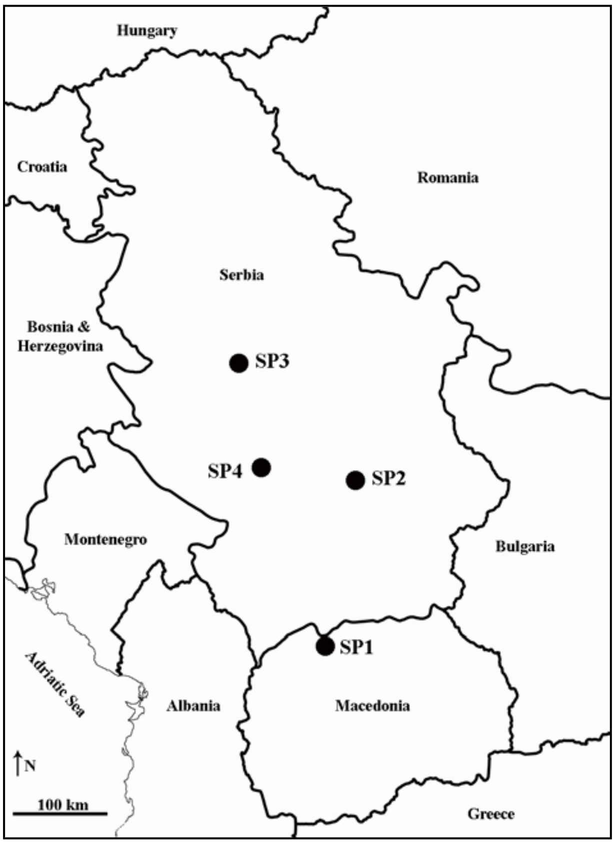

Figure 1. Map of Serbia and Republic of Macedonia with marked locations (SP1–SP4) of the studied populations of *Goniolimon tataricum* (black circles)

The samples were taken from Serbia (Hisar hill, Mt Vujan, Rudine hill) and Republic of Macedonia (Raduša) during 2012 and 2013. The sampling sites differ in geological substrate, having in common high proportion of magnesium. The geological substrate on the sampling sites on Mt Vujan (Brković et al., 1977) and in Raduša (Petkovski et al., 1984) is serpentinite, on Rudine hill harzburgite (Grupa autora, 1970) and dolomitic marble on Hisar hill (Grupa autora, 1969; Ranđelović & Ružić 1986).

The Hisar hill near Prokuplje belongs to the internal Vardar subzone (Vardar zone) and is made up of the Precambrian lower metamorphic complex of metamorphic dolomite (dolomitic marble). In the largest extent, this area is edged by fine-grained gneisses of the same age, which are otherwise dominant in this whole area (Grupa autora, 1969). The youngest formations are Quaternary and are represented by alluvials, which are found along the course of the River Toplica.

The "Vujan" sample site belongs to the Jadar block of the Vardar zone. It is made up of Jurassic serpentinite formed mainly of olivine and piroxene. Although relatively large and compact, within this serpentinite mass, in several places appear igneous rocks of the same age, like diabase, spilite and melaphyre, which is quite clearly on the vertical profile of the area, as well as lower Miocene basal conglomerates. While in the south serpentinite area borders with lower to middle Miocene sandstone, shale, tuffaceous sandstone, marlstone and marly limestone, on the west are only those of middle Miocene age. On the east there are Jurassic olivine gabbro and Late Cretaceous sandstone (in the lesser extent), while to the north it borders with Tertiary marlstone, shale, dolomite and conglomerate (Brković et al., 1977).

"Raduša" sample site is made up of Jurassic serpentine of significant thickness. This small portion of serpentinite is surrounded by harzburgites and dunite of the same age, which occupy a greater area. Significant surface in the close surroundings of the sample site is occupied by Triassic massive marbleized limestone, phyllite and Late Cretaceous (turon-senonian) flysch (Petkovski et al., 1984).

The Rudine hill belongs to the Kopaonik block of the Vardar zone. It is made up of Triassic harzburgite, an ultramafic plutonic rock. The area under harzburgites on the right bank of the Ibar River (where the hill Rudine is located) are relatively small, especially compared to surface that occupy the left river bank (Grupa autora, 1970). The harzburgites of this sample site are edged mostly with the Tertiary volcanic rocks are made up of dacite–andesites, quartzlatite, basaltoids (to a lesser extent), as well as volcanic pyroclastics represented by volcanic breccias, tuffs and agglomerates (Miladinović et al., 2012). The youngest formations are Quaternary and are represented by alluvials, which are found along the course of the Ibar. They are made up of sands, gravels and clays.

Voucher specimens are deposited in BEOU (Herbarium of University of Belgrade). Voucher numbers and collecting details are given in table 1 and figure 1.

2.1. Soil analysis

Soil samples (approximately 500 g per sample) were taken from the rhizosphere of several *G. tataricum* plants and oven dried at 40^{o}C for 3 days, then grinded, sieved through 50 µm sieve and oven dried at constant temperature of 40°C.

Actual and exchangeable pH of soil was measured in distilled water and in 1 M solution of KCl, in a solid-liquid (S/L) ratio of 1:2.5 mL/g (McKeague, 1978). In AL solution (0.1 M ammonium lactate and 0.4 M acetic acid) extract (S/L 1:20) were determined available P_2O_5 and K_2O (Egnér et al., 1960). For determination of phosphate concentration we used molybdenum blue method and flame emission spectrophotometry by Pye Unicam SP 192 atomic absorption spectrophotometer for concentration of potassium. In 1 M ammonium acetate extract (S/L 1:50) (Van Reeuwijk, 2002) were measured available Ca and Mg using atomic absorption spectrophotometry (Shimadzu AA 7000). Determination of organic C concentration was done by dichromate digestion based on FAO procedure (FAO, 1974). Extraction of available metals in soil was performed by 0.05 M EDTA (S/L 1:10) (McGrath, 1996). For total metal extraction, material was digested by HCl and HNO_3 digestion (ISO 11466, 1995). In both extracts concentrations of metals were measured using atomic absorption spectrophotometry (ISO 11047, 1998) (Shimadzu AA 7000).

2.2. Plant Analysis

Plant samples, collected in 5 – 10 replicates of each investigated population, were separated into roots and shoots. After washing carefully with distilled water to remove soil particles, material was oven dried at 40°C for 3 days to obtain dry weights.

Dried and ground plant material was digested using a boiling mixture of 10 mL of nitric and 5 mL of sulphuric acids. After that, solutions were filtered and adjusted to 25 mL with bideionized water. Concentration of phosphorus was determined by modified molybdenum blue method (Chen et al., 1956). Potassium concentration was determined using flame emission spectrophotometry (Shimadzu AA 7000). The series of standard solutions for metals were made from 1 g/L solution purchased from Carlo Erba, Italy, and concentration of metals were determined using atomic absorption spectrophotometry (Shimadzu AA 7000).

2.3. Data analysis

All the measurements data were subjected to a statistical analysis. We used nonparametric statistics since the data were not normally distributed. Arithmetic means and standard deviations are given in tables 2&3. Inter-relationships between the investigated metal concentrations in the soils, roots and shoots were examined using correlation matrices. Correlations were estimated using the bi-variation method, with two-tailed significance and Spearman R correlation coefficients, and only for the elements with concentration > 0.1 mg/kg. All statistical analyses were carried out using the package Statistica 5.1 for Windows (StatSoft, 1997).

Table 1. Characterization of the sampling points of *Goniolimon tataricum* used in this study

Species	Location	Sample point	Lat. (N)	Long. (E)	Alt. (m)	Vegetation alliance	Type of rocks	Voucher Number
G. tataricum	Republic of Macedonia Skopje (Raduša)	SP1	42.0514	21.2548	315	*Centaureo-Bromion fibrosi*	metamorphic ultramafic (serpentinite)	38495
G. tataricum	Serbia Prokuplje (Hisar hill)	SP2	43.2249	21.5768	340	*Scabioso-Trifolion dalmatici*	metamorphic dolomite (dolomitic marble)	34926
G. tataricum	Serbia Gornji Milanovac (Mt Vujan)	SP3	43.9851	20.4441	500	*Chrysopogoni-Danthonion alpinae*	metamorphic ultramafic (serpentinite)	34923
G. tataricum	Serbia Raška (Rudine hill)	SP4	43.2821	20.6420	591	*Centaureo-Bromion fibrosi*	igneous ultramafic (harzburgite)	34925

Table 2. pH, organic C, concentrations (mg/kg) of P_2O_5, K_2O, major elements (Ca, Mg, Fe), and trace elements (Mn, Ni, Zn, Cu, Cr, Co, Cd, Pb) in soils samples. Concentrations are given as means ± standard deviations

	SP1	SP2	SP3	SP4
pH soil in H_2O	6.72	6.96	5.99	6.06
pH soil in 1 N KCl	5.85	6.34	5.2	5.22
Organic C %	5.09 ± 0.48	11.3 ± 0.58	10.4 ± 2.71	16.5 ± 1.42
P_2O_5 (available)	79.2 ± 7.22	858 ± 14.4	41.7 ± 26.0	53.3 ± 5.77
K_2O (available)	384 ± 3.24	413 ± 6.82	446 ± 20.2	481 ± 21.2
Ca (available)	1738 ± 41.6	12322 ± 494	1567 ± 188	2191 ± 53.9
Mg (avaliable)	1075 ± 23.0	368 ± 30.5	2148 ± 43.6	2317 ± 16.2
Ca/Mg	1.62	33.4	0.73	0.95
Fe (total)	59975 ± 2664	21619 ± 890	76595 ± 11890	70609 ± 2128
Fe (available)	278 ± 15.9	74.1 ± 1.44	539 ± 13.2	435 ± 4.35
Mn (total)	1525 ± 12.6	718 ± 26.3	1948 ± 332	1626 ± 70.2
Mn (available)	486 ± 11.1	107 ± 5.18	365 ± 11.9	435 ± 11.2
Ni (total)	1990 ± 33.1	38.7 ± 5.61	2546 ± 424	1828 ± 69.5
Ni (available)	104 ± 1.7	1.08 ± 0.07	209 ± 4.56	187 ± 5.71
Zn (total)	64.5 ± 1.44	345 ± 12.8	141 ± 38.8	105 ± 19.2
Zn (available)	5.02 ± 0.26	48.4 ± 0.8	16.4 ± 0.48	4.89 ± 0.21
Cu (total)	13.6 ± 0.33	23.9 ± 0.52	13.6 ± 2.72	20.4 ± 0.25
Cu (available)	3.74 ± 0.02	4.54 ± 0.49	3.74 ± 0.33	4.7 ± 0.15
Cr (total)	461 ± 12.6	96.8 ± 7.27	898 ± 125	847 ± 60.8
Cr (available)	0.86 ± 0.39	0.1 ± 0.39	0.56 ± 0.36	0.02 ± 0.42
Co (total)	113 ± 2.44	14.6 ± 1.01	172 ± 37. 8	130 ± 0.88
Co (available)	30.4 ± 2.78	0.13 ± 0.14	26.0 ± 4.3	21.2 ± 4.67
Cd (total)	1.86 ± 0.08	2.91 ± 0.08	2.05 ± 0.44	1.95 ± 0.09
Cd (available)	0.33 ± 0.03	1.25 ± 0.01	0.24 ± 0.03	0.38 ± 0.02
Pb (total)	68.4 ± 3.97	122 ± 2.18	67.9 ± 12.3	210 ± 3.1
Pb (available)	24.2 ± 0.51	32.4 ± 0.48	12.5 ± 0.27	82.7 ± 1.9

The translocation factor ($TF=C_{shoot}/C_{root}$) was calculated from the concentration of heavy metals to evaluate plant ability to translocate them from root to the aerial parts (Mattina et al., 2003). Bioaccumulation factor which shows the overall efficiency of plant to accumulate heavy metal in both shoots and roots was calculated based on the plant extractable level of heavy metals in the soil. It is defined as the ratio of shoot or root heavy metals concentration to the available heavy metals concentration in soil.

3. RESULTS

3.1. Soil characteristics

Chemical characteristics of the soil (pH in H_2O, pH in 1 M KCl, percentage of organic matter, and concentrations of P, K), available concentrations of major elements (Fe, Ca, Mg) as well as trace element concentrations are shown in table 2. The pH in H_2O of the soil samples varied from slightly acidic to almost neutral, while pH in 1 M KCl was acidic to moderate acidic. Regarding the concentration of essential macronutrient, content of P varied in a great extent, while the concentrations of K are quite uniform.

As for the major elements concentrations in soil samples, it was determined that the soils had moderate available Ca concentration in ultramafics and very high in dolomitic and low to moderate concentration of available Mg. The available Ca/Mg ratios in 4 soil samples varies, depending on type of substrate, from relatively low in ultramafics to very high in dolomitic ones. Total and available concentrations of trace elements are mainly increased in soil samples from ultramafics (Ni, Cr, Co) or in all samples like for Cd, Mn, Pb, Zn. Only concentrations of Cu are within average values for uncontaminated soils.

3.2. Chemical composition of plant material

Concentration of major elements (Ca, Mg and Fe) in roots and shoots of investigated plant populations are given in table 3. Concentrations of Ca in roots and shoots are generally low in both roots and shoots. On the contrary, Mg is found in extremely high concentrations, significantly higher than in soil (up to 30 times in samples from dolomite). As a result of these Ca and Mg amounts, their ratio is low in both roots and shoots. Although the contents of Fe in roots and shoots are higher than those available in soils, these concentrations do not exceed 800 mg/kg.Trace elements concentration (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in roots and shoots of four analysed populations of *G. tataricum* are shown in table 3. Generally, concentration of Mn and Ni are relatively low; in samples from Raduša and Hisar are higher in shoots, and from Mt Vujan and Rudine hill in roots.

Concentrations of Zn are relatively low with slight variations in roots and shoots. Cu concentrations varied from very low to high, but higher in the roots. Concentrations of Cr and Cd are higher in roots than in shoot in all samples. For Cr they varied from low to relatively high, while concentrations of Cd are low in all samples, with values bellow 2 mg/kg. Contents of Co are greater in shoots than in roots in all analysed populations, in both cases with slight variations. Concentrations of Pb varied to some extent, but they are similar in roots and shoots.

Table 3. Concentration (mg/kg) of major elements (Ca, Mg, Fe), and trace elements (Mn, Ni, Zn, Cu, Cr, Co, Cd, Pb) in *Goniolimon tataricum* plant tissues. Concentrations are given as means ± standard deviations

	SP1	SP2	SP3	SP4
Ca (root)	1008 ± 212	4866 ± 645	2998 ± 377	2204 ± 404
Ca (shoot)	2579 ± 589	2851 ± 1212	1750 ± 179	3764 ± 851
Mg (root)	7511 ± 1155	7109 ± 578	10851 ± 403	7865 ± 350
Mg (shoot)	16584 ± 1008	10137 ± 327	9503 ± 236	16182 ± 1372
Ca/Mg (root)	0.13	0.68	0.28	0.28
Ca/Mg (shoot)	0.16	0.28	0.18	0.23
Fe (root)	337 ± 6.87	195 ± 10.7	692 ± 27.4	492 ± 20.5
Fe (shoot)	787 ± 110	304 ± 11.8	230 ± 5.41	160 ± 26.8
Mn (root)	15.8 ± 0.04	17.0 ± 0.31	25.0 ± 0.29	18.1 ± 0.29
Mn (shoot)	26.2 ± 3.49	20.2 ± 0.73	12.3 ± 0.04	11.4 ± 0.38
Ni (root)	15.8 ± 0.07	1.14 ± 0.71	50.7 ± 2.06	26.8 ± 0.59
Ni (shoot)	33.7 ± 3.21	3.9 ± 0.85	14.0 ± 1.07	10.5 ± 0.94
Zn (root)	8.61 ± 0.39	10.5 ± 0.35	9.21 ± 4.32	18.2 ± 0.62
Zn (shoot)	13.4 ± 2.31	20.5 ± 6.36	10.9 ± 3.6	11.5 ± 2.64
Cu (root)	47.3 ± 1.09	27.6 ± 0.76	44.5 ± 2.57	321 ± 6
Cu (shoot)	39.6 ± 11.5	3.57 ± 0.28	38.5 ± 2.1	2.9 ± 0.28
Cr (root)	71.4 ± 43.5	50 ± 35.7	57.1 ± 18.9	52.4 ± 14.9
Cr (shoot)	33.3 ± 25.1	38.1 ± 29.7	21.4 ± 21.4	71.4 ± 32.7
Co (root)	1.35 ± 0.77	1.52 ± 0.17	2.82 ± 0.54	2.42 ± 0.2
Co (shoot)	5.29 ± 2.31	3.89 ± 1.03	4.22 ± 1.18	3.77 ± 0.78
Cd (root)	1.38 ± 0.25	1.83 ± 0.13	1.41 ± 0.65	0.57 ± 0.41
Cd (shoot)	0.1 ± 0.33	0.11 ± 0.31	< 0.1	< 0.1
Pb (root)	2.62 ± 1.49	5.48 ± 1.8	10.7 ± 1.89	13.1 ± 1.09
Pb (shoot)	2.14 ± 1.43	7.62 ± 3.67	12.9 ± 3.98	15.2 ± 3.67

Table 4. Correlation coefficients (r) for soil; significant correlation coefficients are marked (*p< 0.05, **p< 0.01, ***p< 0.001)

	Cu	Cr	Ni	Zn	Co	Cd	Fe	Mn	Pb	Ca	Mg
Cu	1	-0.42	-0.87***	0.57	-0.57	0.79**	-0.44	-0.52	0.77**	0.79**	-0.35
Cr	-0.42	1	0.65*	-0.27	0.89***	-0.39	0.89***	0.93***	-0.03	-0.58*	0.79**
Ni	-0.87***	0.65*	1	-0.42	0.77**	-0.52	0.68*	0.73**	-0.66*	-0.94***	0.38
Zn	0.57	-0.27	-0.42	1	-0.22	0.66*	-0.24	-0.21	0.22	0.45	-0.36
Co	-0.57	0.89***	0.77**	-0.22	1	-0.41	0.94***	0.97***	-0.2	-0.69*	0.76**
Cd	0.79**	-0.39	-0.52	0.66*	-0.41	1	-0.27	-0.38	0.51	0.51	-0.44
Fe	-0.44	0.89***	0.68*	-0.24	0.94***	-0.27	1	0.96***	0.01	-0.63*	0.83***
Mn	-0.52	0.93***	0.73**	-0.21	0.97***	-0.38	0.96***	1	-0.16	-0.66*	0.8**
Pb	0.77**	-0.03	-0.66*	0.22	-0.2	0.51	0.01	-0.16	1	0.61*	0.23
Ca	0.79**	-0.58*	-0.94***	0.45	-0.69*	0.51	-0.63*	-0.66*	0.61*	1	-0.31
Mg	-0.35	0.79**	0.38	-0.36	0.76**	-0.44	0.83***	0.8**	0.23	-0.31	1

3.3. Relationships between metal concentrations

The results of correlation analysis in soils indicate that five elements (Fe, Mg, Co, Cr and Mn) display a statistically most significant positive correlation with each other (Table 4), while Ni shows the most significant negative correlation with Ca and Cu.

In roots of *G. tataricum*, the most significant positive correlation was between Ni and Fe (Table 5), and the most significant negative correlations were between Cu and Cd.

In shoots of *G. tataricum*, Mn and Fe display statistically the most significant positive correlation (Table 5), while these two elements show the most significant negative correlation with Pb.

The translocation (TF) and accumulating factor (AF) calculated for *G. tataricum* are presented in table 6.

The values indicate good efficiency in translocation of Co, Zn, Ni and Fe. Particularly noteworthy is the movement of Co. Intermediate values were determined for Cr, and the lowest for Cu, where small amount of Cu reached the shoots. In *G. tataricum* especially pronounced tendency in accumulating Cr was observed, with AF in the range between relatively high to extremely high. High accumulation of Cu in most of the samples was registered, as well as high accumulation of Co in the sample from Hisar (dolomitic substrate).

4. DISCUSSIONS

Macronutrients and trace metals content in plants mostly depends on their concentrations and forms in soil solutions, the movement to roots, and further to the aerial parts of the plant. Plant uptake is directly correlated to "plant available" concentrations (extractable fractions), not to total soil metal concentration (Adriano et al., 2001).

Regarding the macronutrients, concentration of calcium in ultramafics are the lowest in soils, while in dolomitic these concentrations are due to the presence of carbonates very high. Therefore, Ca/Mg ratio in ultramafic soils was expectably low (Proctor & Woodel, 1975; Kruckeberg, 1984; Brooks, 1987; Proctor, 1999), and very high in dolomitic ones. Calcium saturation of ultramafic soil is particulary important. Therefore it is very important ability of ultramafic flora to provide sufficient quantities of this element, given its significant deficiency in soils (Duvigneaud, 1966).

Table 5. Correlation coefficients (r) for *Goniolimon tataricum*. The upper right part refers to the roots, the lower left part refers to the shoots; significant correlation coefficients are marked (*p< 0.05, **p< 0.01, ***p< 0.001)

	Cu	Cr	Ni	Zn	Co	Cd	Fe	Mn	Pb	Ca	Mg
Cu	1	0.09	0.37	0.38	0.3	-0.83***	0.38	0.02	0.43	-0.72**	0.14
Cr	-0.43	1	-0.02	-0.21	0.09	-0.41	-0.01	-0.03	-0.14	-0.14	0.26
Ni	0.63*	-0.16	1	-0.01	0.8**	-0.37	1***	0.78**	0.59*	-0.22	0.71*
Zn	0.06	0.27	-0.26	1	0.05	-0.15	0	0.16	0.59*	0.07	-0.18
Co	0.19	0.26	0.3	0.25	1	-0.5	0.81**	0.82**	0.7*	0.06	0.79**
Cd	0.25	0.01	0.04	0.14	0.39	1	-0.37	-0.13	-0.45	0.6*	-0.25
Fe	0.49	-0.37	0.4	0.3	0.26	0.27	1	0.78**	0.58*	-0.22	0.73**
Mn	0.48	-0.41	0.4	0.31	0.2	0.18	0.99***	1	0.77**	0.38	0.67*
Pb	-0.46	0.3	-0.25	-0.34	-0.02	-0.15	-0.83***	-0.82***	1	0.14	0.35
Ca	-0.58*	0.36	-0.22	0.31	-0.33	-0.22	-0.23	-0.18	0.12	1	0.09
Mg	-0.36	0.28	0.31	0	0.17	0.18	0.24	0.24	-0.16	0.59*	1

Table 6. Accumulation potential of *Goniolimon tataricum* for Fe and selected trace elements (Ni, Zn, Cu, Cr, Co)

Sample point	Fe r/s	Fe TF	Fe AF	Ni r/s	Ni TF	Ni AF	Zn r/s	Zn TF	Zn AF	Cu r/s	Cu TF	Cu AF	Cr r/s	Cr TF	Cr AF	Co r/s	Co TF	Co AF
Raduša	1.21	2.33	2.83	0.15	2.13	0.32	1.72	1.55	2.66	12.6	0.84	10.6	83.1	0.47	38.8	0.04	3.92	0.17
Hisar hill	2.64	1.56	4.1	1.06	3.42	3.61	0.22	1.95	0.42	6.07	0.13	0.79	500	0.76	381	11.7	2.56	29.9
Mt Vujan	1.28	0.33	0.43	0.24	0.28	0.07	0.56	1.19	0.67	11.9	0.86	10.3	102	0.38	38.3	0.11	1.5	0.16
Rudine hill	1.13	0.33	0.37	0.14	0.39	0.06	3.72	0.63	2.36	68.4	0.01	0.62	2619	1.36	3571	0.11	1.56	0.18

In contrast to Ca, elevated concentrations of Mg are characteristic not only for ultramafics, but also for dolomites (Jones, 1951; McHale & Winterhalder, 1997; Mota et al., 2008). Considering this common features, the presence of same species on ultramafic and dolomitic substrates is not an unusual finding (Perez-Latorre et al., 2013). High tolerance towards Mg and substantial accumulation of this element in G. tataricum populations inhabiting ultramafic and dolomites may be an evolutionary trait inherited from a common predecessor. Although our results show low concentration of available Mg in the dolomitic versus the ultramafic sites, it should be borne in mind that dolomite is very rich in $MgCO_3$ which is slowly and constantly solubilized by low pH plant exudates in the rhizosphere, making thus large Mg quantities available to the plants during longer time intervals. High requirements for Mg may have evolved to protect plants from harmful effects of heavy metals. By acquiring Mg, uptake of other metals sharing the same channels and transporters (e.g. Ni, Co, Fe, Mn, Cu) (Li et al., 2001) is inhibited. Besides, high concentration of Mg in plant tissue, especially in shoots, prevents incorporation of other metals in chlorophyll molecules. Also, Mg is needed as a co-factor of ATP-ases responsible for glutathione-mediated transport of heavy metals to vacuoles (Salt & Rauser, 1995).

A low content of macronutrients was expected in ultramafic soils (Walker, 1954; Kruckeberg, 1984; Brooks, 1987; Proctor, 1999). Concentrations of K are comparatively low, similarly to the Balkan ultramafics (Bani et al., 2010), although in all the samples they are higher than those reported by Tumi et al. (2012) and Tomović et al., (2013) for other ultramafic soils of Serbia. Similar to potassium, the amounts of phosphorus are low and elevated only on dolomitic soils. The concentrations of Fe in the ultramafic samples, both total and available, are very high and correspond to a great extent to those determined in ultramafics of the Balkan Peninsula, i.e. Albania, Greece and Bulgaria (Bani et al., 2010). Concentrations of Fe in dolomitic soil are remarkably lower.

Increased concentrations of trace elements, in particular Mn, Ni, Cr and Co, were expected in samples from ultramafics based on previous findings in Serbia (Tumi et al., 2012), Albania, Bulgaria, Greece (Bani et al., 2010), Portugal (Freitas et al., 2004), Turkey (Reeves et al., 2009) and Iran (Ghaderian et al., 2007). Concentration of Ni in dolomitic sample, remarkably lower in comparison to ultramafics, is also more than 10 times lower comparing to those from dolomite in South Africa (Dowding & Fey, 2007) with Ni amounts in the range 399–491 mg/kg. Contents of Mn in soil samples from ultramafics of Serbia and Republic of Macedonia are within the values obtained from the similar substrate from Serbia (Tumi et al., 2012), Albania, Greece, Bulgaria (Bani et al., 2010) and Iran (Ghaderian et al., 2007). The Mn content in dolomitic, although higher than the average (411 to 550 mg/kg) (Kabata-Pendias, 2011) is still much lower than in the ultramafics. The concentrations of chromium are also one of the important indicators of the substrate on which the soil develops. Soils developed from the ultramafics are especially rich in Cr, sometimes to above 100,000 mg/kg (Kabata-Pendias, 2011). In our samples these amounts are similar to those from ultramafic of Serbia (Tumi et al., 2012, Tomović et al., 2013), but lower than those from Greece and Bulgaria (Bani et al., 2010). In dolomitic samples these concentrations were lower, but still remains higher than the average world values (60 mg/kg) (Kabata-Pendias, 2011), and even in the range of values obtained from the ultramaficsof Iran (Ghaderian et al., 2007). The concentrations of Co in the ultramafic soils are elevated and correspond to those determined in samples of the analog substrate in Serbia (Tumi et al., 2012), Albania, Greece and Bulgaria (Bani et al., 2010), Portugal (Freitas et al., 2004) and Turkey (Reeves et al., 2009). In dolomitic soils these values are within range of average world values (Kabata-Pendias, 2011), but considerably lower than those reported by Dowding & Fey (2007), which are within range 169–267 mg/kg.

Concentrations of Ni and Mn in plant tissues are remarkably lower than those available in soils. The lowest concentrations of Ni were observed in dolomitic samples, as expected, although the ability of some species to store Ni could be better related to a protective mechanism against herbivores (Boyd & Martens, 1998; Proctor, 1999; Martens & Boyd, 2002) than to adaptation to ultramafic. The highest concentrations of Cr were in the roots of *G. tataricum*, up to 100 times higher compared to soil available quantities. Golovatyj et al., (1999) showed that the maximum Cr contents were in the roots and the minimum in the vegetative and reproductive organs. As it was already found by Lombini et al., (1998), Bani et al., (2010), Tumi et al., (2012), Tomović et al., (2013), concentrations of Co in the ultramafic soils in comparison with plant tissues are remarkably higher. However, such relation is not observed in soil samples from dolomites.

Increased concentrations of Zn, Cd and Pb in dolomitic soil were reported by Trakal et al., (2011) also. The contents of Cd from the ultramafic soil samples were similar to those reported by Tumi et al. (2012), and generally higher than the average world value (Kabata-Pendias, 2011). The obtained concentrations of Zn were 3–5 times higher on the dolomitic compared to ultramafics, and even two times higher than the value recorded on dolomites of South Africa (Dowding & Fey, 2007). The highest amount of Pb, obtained from ultramafic soil samples from Rudine hill (Serbia) exceeds the values for this substrate type determined Tumi et al., (2012) for several localities in Serbia. Ultramafic concentrations of Cu correspond to those determined for Serbia (Tumi et al., 2012; Tomović et al., 2013), Turkey (Reeves et al., 2009), Bulgaria and Albania (Bani et al., 2010), while the values from dolomites were lower than those reported by Dowding & Fey (2007).

The concentrations of Zn and Pb in the roots and shoots of *G. tataricum* were lower than the available contents of these elements in the soils and generally higher in the shoots, but without any significant variations, while the highest Cd concentrations were found in the roots, with small quantities that reach the shoots. Cu contents were higher in the roots of *G. tataricum* than the available concentration of this element in the corresponding soils, indicating accumulation. Cu accumulation is not so common in higher plants, although high concentrations were found in the roots of the species *Alyssum murale* on the ultramafics of Serbia (Tumi et al., 2012). Elevated quantities of Cu were observed on dolomites also. Therefore, it is possible that the preference for copper is bonded to family Plumbaginaceae, since *Armeria maritima* was recognized as an indicator of copper accumulation (Ernst, 1969; Farrago & Mullen, 1979; Farago et al., 1980; Neumann et al., 1995; Olko et al., 2008).

In general, according to relationships with heavy metal, plants can be grouped into four categories: excluders, indicators, accumulators and hyperaccumulators (Baker, 1981). In order to determine the status of *G. tataricum*, we calculated its accumulation potential (Table 6). Plant ability to accumulate metals from soils can be estimated by using the accumulation factor (AF), i.e. enrichment coefficient, defined as the ratio of metal concentration in the shoots to that available in soil and as the ratio of the metal concentration in the roots to that available in soil. A plant's ability to translocate metals from the roots to the shoots is measured using TF, which is defined as the ratio of shoot/root metal concentration.

Remarkably high AF was noticed for Cr, especially for the plants from Rudine hill (AF=3571). The largest amounts of Cr were retained in the roots, as expected (Golovatyj et al., 1999), except in plant samples from Rudine hill with high accumulation both in the shoots and roots. *Goniolimon tataricum* principally behave as Cr excluder. The reason of the high accumulation in the roots could be immobilization of Cr in the vacuoles of the root cells, which may be a natural toxicity response of the plant (Shanker et al., 2004). Considering the large amount of accumulated Cr, as well as the fact that Fe and Cr are known to compete for carrier binding (Wallace et al., 1976), low concentration of Fe in plant tissues were expected.

According to TF values, *G. tataricum* on dolomites clearly accumulate Co and Zn considering that all values of shoot/root are higher than 1 (Baker, 1981; Baker & Brooks, 1989; Tilstone & Macnair, 1997). There is an obvious tendency of *G. tataricum* to translocate and accumulate high metal concentrations (Co, Zn, and partially Ni, Fe and Mn) in above-ground plant parts from both low and high trace metal concentrations in soil, without toxicity symptoms. Translocation factors higher than 1 indicated a very efficient ability to transport metal from roots to shoots, most likely due to efficient metal transport systems (Zhao et al., 2002).

The values of translocation and accumulation factors showed that the concentrations of Cu in the roots, where Cu is retained, were higher than those available in the soils. The strong capability of root tissues to hold Cu against the transport to shoots was also observed in species *Armeria maritima*, where only 10% of Cu concentration was translocated into the leaves (Neumann et al., 1995).

Analysis of correlations between the contents of investigated elements in the soils, roots and shoots, showed that relationships of Fe with other analysed elements were statistically the most important. Namely, Fe is positively correlated with Cr, Co, Mn and Mg in soils, with Ni in roots, and with Mn in shoots. This is in contradiction with the attitudes that high level of Fe in growth media results in decreasing uptake of several trace elements, mainly Ni and Mn, and that excess amount of Mn, Ni and Co cause a reduction in the absorption and translocation of Fe (Kabata-Pendias, 2011). The close association of many trace elements with Mn oxides is well known (McKenzie, 1980; Dixon & White, 2002; Kabata-Pendias, 2011). It was argued that Co has a particularly high affinity for Mn oxides (Kabata-Pendias, 2011), which was also indicated in our soil analysis. The interactions between Ni and the other trace elements, Fe in particular, is believed to be a common mechanism involved in the Ni toxicity (Kabata-Pendias, 2011). Cataldo et al., (1978) found that the absorption of Ni by soybean roots and its translocation from roots to shoots were inhibited by the presence of Cu, Zn, and Fe, whereas Wallace et al. (1980) stated that Fe did not depress Ni concentrations in leaves of bush beans. It was also determined that due to the activation of the common channels for metal uptake, increase of Ni concentration increased Fe accumulation in plants, primarily in the roots (Narwal et al., 1991; Parida et al., 2003). This is the most probable reason for the uptake of the large quantities of Fe together with Ni in *G. tataricum* and their positive correlation (r = 1) in roots. The interactions between Cd and Cu are also complex. They are both antagonistic and synergistic in element uptake by roots (Kabata-Pendias, 2011). The inhibitory effect of Cu on Cd absorption was reported most often (Olko et al., 2008; Kabata-Pendias, 2011), the same as in *G. tataricum*.

5. CONCLUSIONS

Considering that the samples were collected from two different substrate types, the concentrations of macro- and trace elements vary to a certain extent. The Ca/Mg quotients for the available fraction in ultramafic samples are close to 1, and remarkably high in dolomitic ones. Soil samples collected from ultramafics contained elevated levels of almost all analysed trace elements. As for the dolomitic samples, they are characterized by elevated levels of Cd, Mn, Pb, Zn, and among the macronutrients, especially of Ca.

Despite relatively low available Mg content in the soil samples, the concentrations in plant tissues are extremely high, significantly higher than in soil (especially in dolomitic samples). On the contrary, concentrations of Ca in roots and shoots are generally low. The Ca/Mg ratios in plant tissues from all sample points are <1, as is typical for ultramafics. Concentrations of the majority of trace elements (Mn, Ni, Zn, Pb) were found in plants at lower levels than in the soil. Fe and some of the trace elements like Cd, Cr and Cu, were present in plant tissues in larger quantities than in soil.

These analyses revealed that *G. tataricum* possesses the ability to accumulate Cu, previously observed in other representatives of the family Plumbaginaceae. In addition, strong ability of *G. tataricum* to accumulate Mg and Cr from corresponding soil is very conspicuous. Although *G. tataricum* cannot be characterized as hyperaccumulator of Cr, high AF and low TF make this species suitable for phytostabilization of contaminated sites.

ACKNOWLEDGEMENTS

The authors express their thanks to Lj. Melovski (Faculty of Natural Sciences and Mathematics, Sts. Cyril and Methodius University of Skopje) for his help in collecting plant material in the field. The Ministry of Education, Science and Technological Development of the Republic of Serbia supported this research through Grant 173030 “Plant biodiversity of Serbia and the Balkans – assessment, sustainable use and protection”.

REFERENCES

Abratowska, A., Wąsowicz, P., Bednarek, P.T., Telka, J. & Wierzbicka, M., 2012. *Morphological and genetic distinctiveness of metallicolous and non‐metallicolous populations of Armeria maritima s.l. (Plumbaginaceae) in Poland*. Plant Biology, 14, 4, 586-595.

Adriano, D.C., 2001. *Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals*. New York: Springer-Verlag, p. 867.

Baker, A.J.M., 1981. *Accumulators and excluders - strategies in the response of plant to heavy metals*. Journal of Plant Nutrition, 3, 643-654.

Baker, A.J.M. & Brooks, R., 1989. *Terrestrial higher plants which hyperaccumulate metallic elements. A review of their distribution, ecology and phytochemistry*. Biorecovery, 1, 2, 81-126.

Baker, A.J.M., Proctor, J. & Reeves, R.D., eds., 1992. *Vegetation of ultramafic (serpentine) soils*. Androver, UK: Intercept Ltd, p. 509.

Bani, A., Pavlova, D., Echevarria, G., Mullaj, A., Reeves, R.D., Morel, J.L. & Sulçe, S., 2010. *Nickel hyperaccumulation by the species of Alyssum and Thlaspi (Brassicaceae) from the ultramafic soils of the Balkans*. Botanica Serbica 34, 1, 3-14.

Boyd, R.S. & Martens, S.N., 1998. *The significance of metal hyperaccumulation for biotic interactions*. Chemoecology, 8, 1–7.

Bradshaw, H.D., 2005. *Mutations in CAX1 produce phenotypes characteristic of plants tolerant to serpentine soils*. New Phytologist, 167, 1, 81-88.

Brady, K.U., Kruckeberg, A.R. & Bradshaw, H.D., 2005. *Evolutionary ecology of plant adaptation to serpentine soils*. Annual Review of Ecology and Systematics, 36, 243-266.

Brković, T., Malešević, M., Klisić, M., Urošević, M., Trifunović, S., Radovanović, Z. & Božanić, M., 1977. *Basic geological map of SFRJ 1:100000, Sheet Čačak* (In Serbian). Savezni geološki zavod, Beograd.

Brooks, R.R., 1987. *Serpentine and its vegetation. A* *multidisciplinary approach*. Portland, USA: Dioscorides Press, p. 454.

Buzurović, U., Stevanović, V., Niketić, M., Jakovljević, K. & Tomović, G., 2013. *On the distribution of Goniolimon tataricum (Plumbaginaceae) in Serbia*. Botanica Serbica, 37, 2, 167-172.

Cataldo, D.A., Garland, T.R. & Wildung, R.E., 1978. *Nickel in plants II*. Plant Physiology, 62, 4, 566-570.

Chen, P.S., Toribora, T.Y., Warner, H., 1956. Microdetermination of phosphorus. Analytical Chemistry, 28, 1756-1758.

Dixon, J.B. & White, N.G., 2002. *Manganese Oxides*. In: Dixon, J.B. & Schulze, D.G. editors. Soil Mineralogy with Environmental Applications. USA: Soil Science Society of America, pp. 367–388.

Donahue, R.L., Miller, R.W. & Shickluna, J.C., 1977. *Soils: an introduction to soils and plant growth*. Engelwood Cliff, New Jersey, USA: Prentice Hall, Inc., p. 667.

Dowding, C.E. & Fey, M.V., 2007. *Morphological, chemical and mineralogical properties of some manganese-rich oxisols derived from dolomite in Mpumalanga province, South Africa*. Geoderma, 141, 23-33.

Dudić, B., Rakić, T., Šinžar-Sekulić, J., Atanacković, V. & Stevanović, B., 2007. *Differences of metal concentrations and morpho-anatomical adaptations between obligate and facultative serpentinophytes from Western Serbia*. Archives of Biological Science, 59, 4, 341-349.

Duvigneaud, P., 1966. *Note sur la biogéochimie des serpentines du Sud-Ouest de la France* (In French). Bulletin Société royale de Botanique de Belgique, 99, 271-329.

Đorđević, V., Đorđević, P. & Milovanović, D., 1991. *Basics of petrology* (In Serbian). Nauka, Beograd, p. 223.

Egnér, H., Riehm, H. & Domingo, W.R., 1960. *Untersuchungenüber die chemische Boden analyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor- und Kaliumbestimmung* (In German). Kungl Lantbrukshögskolans Annaler, 26, 199-215.

Ernst, W., 1969. *Pollen analytischer Nachweiseines Schwermetallrasens in Wales*. Vegetatio, 18, 393-400.

Ernst, W.H.O., 1974. *Schwermetallvegetation der Erde*. Stuttgart: Gustav Fisher Verlag, p.194.

Ernst, W.H.O., 1982. *Schwermetallpflanzen*. In: Kinzel H, editor. Pflanzenökologie und Mineralstoffwechsel. Stuttgart, Ulmer, pp. 472–506.

Ernst, W.H.O., 1998. *Effects of heavy metals in plants at the cellular and organismic level*. In: Schuurmann, G., editor. Ecotoxicology: Ecological Fundamentals, Chemical Exposure and Biological Effects. Heidelberg, Wiley, pp. 587-620.

FAO, 1974. *The Euphrates Pilot Irrigation Project. Methods of soil analysis. Gadeb Soil Laboratory (A laboratory manual)*. Food and Agriculture Organization, Rome, Italy, p.40.

Farrago, M.E. & Mullen, W.A., 1979. *Plants which accumulate metals. IV. A possible copper-proline complex from the roots of Armeria maritima*. Inorganica Chimica Acta 32, 93-94.

Farago, M.E., Mullen, W.A., Cole, M.M. & Smith, R.F., 1980. A study of *Armeria maritima* (Mill.) Willdenow growing in a copper-impregnated bog. Environmental Pollution, 21, 3, 225-244.

Freitas, H., Prasad, M.N.V. & Pratas, J., 2004. *Analysis of serpentinophytes from north-east of Portugal for trace metal accumulation–relevance to the management of mine environment*. Chemosphere, 54, 11, 1625-1642.

Ghaderian, S.M., Mohtadi, A., Rahiminejad, M.R. & Baker, A.J.M., 2007. *Nickel and other metal uptake and accumulation by species of Alyssum (Brassicaceae) from the ultramafics of Iran*. Environmental Pollution, 145, 1, 293-298.

Golovatyj, S.E., Bogatyreva, E.N. & Golovatyi, S.E., 1999. *Effect of levels of chromium content in a soil on its distribution in organs of corn plants*.SoilResearch Fertility, 25, 197–204.

Goodwin-Bailey, C.I., Woodell, S.R.J. & Loughman, B.C., 1992. *The response of serpentine, mine spoil and saltmarsh races of Armeria maritima (Mill.) Willd. to each others' soils*. In: Baker, A.J.M., Proctor, J. & Reeves, R.D., editors. Vegetation of ultramafic (serpentine) soils. Intercept Ltd Andover, UK, pp. 375-390.

Greuter, W., Burdet, M.H. & Long, G., 1989. *Med-Checklist **4***. Conservatoire et Jardin botaniques de la Ville de Gèneve, Med-Checklist Trust of OPTIMA, Gèneve, p. 458.

Grupa autora, 1969**.** *Basic geological map of SFRJ 1:100000, Sheet Niš* (In Serbian). Savezni geološki zavod, Beograd.

Grupa autora, 1970**.** *Basic geological map of SFRJ 1:100000, Sheet Novi Pazar* (In Serbian). Savezni geološki zavod, Beograd.

Henwood, W.J., 1857. *Notice of the copper turf of Merioneth*. Edinburgh New Philosophical Journal, 5, 61-63.

ISO 11466, 1995. *International Standard. - Soil quality — extraction of trace elements soluble in aqua regia*: 03–01. Technical Committee ISO/TC 190, Soil quality, p. 6.

ISO 6636/2, 1981. *International Standard: fruits, vegetables and derived products—determination of zinc content—part 2: atomic absorption spectrometric method*. Technical Committee ISO/TC 34, Agricultural food products, p. 11.

Jones, H.T., 1951. *Magnesium as a plant nutrient*. Chemistry & Industry, 15, 1108–1110.

Kabata-Pendias, A., 2011. *Trace Elements in Soils and Plants*. CRC Press,Florida, USA, p. 505.

Köhl, K.I., 1997. *The effect of NaCl on growth, dry matter allocation and ion uptake in salt marsh and inland populations of Armeria maritima*. New

Phytologyst, 135, 2, 213-225.

Kruckeberg, A.R., 1984. *California serpentines: flora, vegetation, geology, soils and management problems*. University of California Press, Berkeley, Publications in Botany, 78, 1-180.

Lefebvre, C., 1974. *Population variation and taxonomy in Armeria maritima with special reference to heavy metal tolerant populations.* New Phytologyst, 73, 1, 209-219.

Li, L., Tutone, A.F., Drummond, R.S.M., Gardner, R.C. & Luan, S., 2001. *A novel family of magnesium transport genes in Arabidopsis*. Plant Cell 13, 2761-2775.

Linčevski, I.A., 1952. *Plumbaginaceae* Lindl. In: Šiškin, B.K. & Bobrov, E.G., editors. Flora SSSR, Vol. 18. Botanicheskij Institut Akademija Nauk SSSR Moskva-Lenjingrad, SSSR, pp. 292-474.

Lombini, A., Dinelli, E., Ferrari, C. & Simoni, A., 1998. *Plant-soil relationships in the serpentinite screes of Mt Prinzera (Northern Apennines, Italy)*. Journal of Geochemical Exploration, 64, 1, 19-33.

Martens, S.N. & Boyd, R.S., 2002. *The defensive role of Ni hyperaccumulation by plants: a field experiment*. American Journal of Botany, 89, 998–1003.

Mattina, M.I., Lannucci-Berger, W., Musante, C. &White, J.C., 2003. *Concurrent plant uptake of heavy metals and persistent organic pollutants from soil*. Environmental Pollution, 124, 3, 375-378.

McGrath, D., 1996. *Application of single and sequential extraction procedures to polluted and unpolluted soils*. Science of the Total Environment, 178, 37-44.

McHale, D. & Winterhalder, K., 1997. *The importance of the calcium–magnesium ratio of the limestone used to detoxify and revegetate acidic, nickel- and copper-contaminated soils in the Sudbury, Canada mining and smelting areas.* In: Jaffré, T.J., Reeves, R.D. & Becquer, T., editors. The Ecology of Ultramafic and Metalliferous Areas. Proceedings of the 2nd International Conference on Serpentine Ecology, Nouméa, Centre ORSTOM de Nouméa, pp. 267–273.

McKeague, J.A., 1978. *Manual on soil sampling and methods of analysis*. Canadian Society of Soil Science, Ottawa, Canada, pp. 66-68.

McKenzie, R.M., 1980. *The adsorption of lead and other heavy metals on oxides of manganese and iron.* Australian Journal of Soil Research, 18, 1, 61-73.

Micevski, K &Matevski, V., 1995. *Goniolimon Boiss*. In: Micevski, K., editor. Flora na Republika Makedonija, Vol. 1. Makedonska akademija na naukite i umetnostite, Skopje, pp. 480-482.

Miladinović, B., Papić, P. & Mandić, M., 2012. *Groundwater pollution with heavy metals in the Ibar alluvium near Raška (Serbia).* Geoloski anali Balkanskoga poluostrva, 73, 125-130.

Mota, J.F., Medina-Cazorla, J.M., Navarro, F.B., Pérez-García, F.J., Pérez-Latorre, A., Sánchez-Gómez, P., Tores, J.A., Benavente, A., Blanca, G., Gil, C., Lorite, J., Merlo, M.E., 2008. *Dolomite flora of the Baetic ranges glades (South Spain).* Flora, 203, 5, 359-375.

Narwal, R.P., Singh, M. & Singh, J.P., 1991. *Effect of Ni enriched sewage water on the accumulation of Ni and other heavy metals in corn*. Journal of the Indian Society of Soil Science, 39, 1, 123-128.

Neely, E.E. & Barkworth, M.E., 1984. *Vegetation on soils derived from dolomite and quartzite in the Bear River Range, Utah: a comparative study*. Bulletin of the Torrey Botanical Club, 111, 2, 179-192.

Neumann, D., Nieden, U.Z., Lichtenberger, O. & Leopold, I., 1995. *How Does Armeria maritima Tolerate High Heavy Metal Concentrations?* Journal of Plant Physiology, 146, 5, 704-717.

Obratov-Petković, D., Bjedov, I. & Belanović, S., 2008. *The content of heavy metals in the leaves of Hypericum perforatum L. on serpentinite soils in Serbia*. Bulletin of the Faculty of Forestry, 98, 143–154.

Olko, A., Abratowska, A., Zylkowska, J., Wierbicka, M. & Tukiendorf, A., 2008. *Armeria maritima from a calamine heap—Initial studies on physiologic–metabolic adaptations to metal-enriched soil*. Ecotoxicology and Environmental Safety, 69, 209–218.

Palache, C., Bernman, H. & Frondel, C., 1951. *Dana's system of mineralogy (7th edition), vol II*. John Wiley and Sons, New York, NY, p. 187.

Parida, B.K., Chhibba, I.M. &Nayyar, V.K., 2003. *Influence of nickel-contaminated soil on fenugreek (Trigonella corniculata L.) growth and mineral composition*. Scientia Horticulturae, 98, 2, 113-119.

Pavlova, D.K., 2001. *Mountain vegetation on serpentine areas in Bulgarian Eastern and Central Rhodope Mts – ecology and conservation*. In: Radoglou, K., editor. Proceedings of the International Conference, Forest Research: A challenge for an integrated European approach, Vol. 1. NAGREF-Research Forest Institute, Thessaloniki, pp. 227–232.

Pavlova, D.K., Kožuharova, E.K. & Dimitrov, D.S., 1998. *The serpentine flora in the eastern Rhodopes mountains (Bulgaria).* In: Tsekos, I. & Moustakis, M., editors. Progress in botanical research, Proceedings of the 1st Balkan Botanical Congress. Kluwer Academic Publishers, Dordrecht, pp. 133–136.

Pefrov, V.P., 1980. *Magnesite deposits of Serbia and their origin*. International Geology Review, 22, 5, 497-510.

Perez-Latorre, A.V., Hidalgo-Triana, N. & Cabezudo, B., 2013. *Composición, ecología y conservación de la flora serpentínica suribérica en el contexto de la cuenca mediterránea*. Anales del Jardín Botánico de Madrid, 70, 1, 62-71.

Petkovski, P., Popovski, S. & Karovik, J., 1984. *Basic* *geological map of SFRJ 1:100000, Sheet Kačanik* (In Serbian). Savezni geološki zavod, Beograd.

Proctor, J., 1999. *Toxins, nutrient shortages and droughts: the serpentine challenge*. Trends in Ecology & Evolution, 14, 9, 334– 335.

Proctor, J. & Woodel, S.R.J., 1975. *The ecology of serpentine soils*. Advances in Ecological Research, 9, 255–366.

Ranđelović, N. & Ružić, M., 1986. *Dolomite pasture vegetation in southeastern Serbia* (In Serbian). Ekologija, 21, 2, 75-91.

Reeves, R.D., Adigüzel, N. & Baker, A.J.M., 2009. *Nickel Hyperaccumulation in Bornmuellera kiyakii Aytaç & Aksoy and associated plants of the Brassicaceae from Kızıldağ (Derebucak, Konya-Turkey)*. Turkish Journal of Botany, 33, 1, 33-40.

Roberts, B.A. & Proctor, J., 1992. *The ecology of areas with serpentinized rocks. A world view*. Kluwer Academic Publishers, Dordrecht, p. 427.

Rosen, O., Desmons, J. & Fettes, D., 2011. *Metacarbonate and related rocks*. In: Fettes, D. & Desmons, J. editors. Metamorphic Rocks: A Classification and Glossary of Terms. Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Metamorphic Rocks. Cambridge University Press, Cambridge, pp. 46-50.

Rostański, A. & Wierzbicka, M., 2002. *Microevolutionary changes in ecotypes of calamine waste heap vegetation near Olkusz, Poland: a review*. Acta Biologica Cracoviensia, 44, 7-19.

Salt, E. & Rauser, W.E., 1995. *MgATP-dependent transport of phytochelatines across the tonoplast of oat roots*. Plant Physiology, 107, 1293-1301.

Sequeira, E.M. & Pinto da Silva, A.R., 1992. *Ecology of serpentinized areas of north-east Portugal*. In: Roberts, B.A. & Proctor, J., editors. The ecology of areas with serpentinized rocks. Kluwer Academic Publishers, Dordrecht, pp. 169-197.

Shanker, A.K., Djanaguiraman, M., Sudhagar, R., Chandrashekar, C.N. & Pathmanabhan, G., 2004. *Differential antioxidative response of ascorbate glutathione pathway enzymes and metabolites to chromium speciation stress in green gram (Vigna radiata (L.) R. Wilczek, cv CO4) roots*. Plant Science, 166, 4, 1035–1043.

Skinner, H.C.W., 2005. *The Web of Magnesium*. International Geology Review, 47, 1111-1119.

Stevanović, V., Tan, K. & Iatrou, G., 2003. *Distribution of the endemic Balkan flora on serpentine I. – obligate serpentine endemics*. Plant Systematics and Evolution, 242, 1-4, 149-170.

Tilstone, G.H. & Macnair, M.R., 1997. *The Consequence of Selection for Copper Tolerance on the Uptake and Accumulation of Copper in Mimulusguttatus*. Annals of Botany, 80, 6, 747-751.

Tomović, G., Mihailović, N., Tumi, A.F., Gajić, B.A., Mišljenović, T. & Niketić, M., 2013. *Heavy metals in soils and several Brassicaceae plants of serpentine sites of Serbia*. Archives of Environmental Protection, 39, 4, 29-49.

Trakal, L., Neuberg, M., Tlustoš, P., Száková, J., Tejnecký, V. & Drábek, O., 2011. *Dolomite limestone application as a chemical immobilization of metal-contaminated soil*. Plant, Soil and Environment, 57, 4, 173-179.

Tumi, A.F., Mihailović, N., Gajić, B.A., Niketić, M. & Tomović, G., 2012. *Comparative study of hyperaccumulation of nickel by Alyssum murale s.l. populations from the ultramafics of Serbia*. Polish Journal of Environmental Studies, 21, 6, 1855-1866.

Van Reeuwijk, L.P., 2002. *Procedures for Soil Analysis. 6th ed.* ISRIC Technical Paper 9, Wageningen, p.120.

Vinterhalter, B., Savić, J., Platiša, J., Raspor, M., Ninković, S., Mitić, N. & Vinterhalter, D., 2008. *Nickel tolerance and hyperaccumulation in shoot cultures regenerated from hairy root cultures of Alyssum murale Waldst. et Kit*. Plant Cell Tissue and Organ Culture, 94, 3, 299-303.

Vinterhalter, B. & Vinterhalter, D., 2005. *Nickel hyperaccumulation in shoot cultures of Alyssum markgrafii*. Biologia Plantarum, 49, 121-124.

Wallace, A., Romney, E.M., Mueller, R.T. & Alexander, G.V., 1980. *Calcium-trace metal interactions in soybean plants*. Journal of Plant Nutrition, 2, 1-2, 79-86.

Wallace, A., Soufi, S.M., Cha, J.W. & Romney, E.M., 1976. *Some effects of chromium toxicity on bush bean plants grown in soil*. Plant Soil, 44, 2, 471–473.

Walker, R.B., 1954. *The ecology of serpentine soils II. Factors affecting plant growth on serpentine soils*. Ecology, 35, 2, 259-266.

Walker, R.B., 2001. *Low molybdenum status of serpentine soils of western North America*. South African Journal of Science, 97, 565-568.

Wyckoff, R.W.G. & Merwin, H.E., 1924. *The crystal structure of dolomite*. American Journal of Science, 48, 447-461.

Zhao, F.J., Hamon, R.E., Lombi, E., McLaughlin, M.J. & McGrath, S.P., 2002. *Characteristics of cadmium uptake in two contrasting ecotypes of the hyperaccumulator Thlaspi coerulescens*. Journal of Experimental Botany, 53, 368, 535-543.

Received at: 14. 04. 2014

Revised at: 16.12. 2014
Accepted for publication at: 13. 01. 2015
Published online at: 21. 01. 2015